SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY AND
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THE SOLID PHASE FUNCTIONAL GROUP APPROACH TO OIL SHALE ANALYSIS

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ABSTRACT

Two classes of solid phase reagents have been devised to deal with the analysis of the soluble organic phases derived from oil shales (bitumens and tars). In the first-the solid phase organic functional group reagents-specific organic functional chromogenic reagents, bound to a solid matrix, were devised to determine the functional groups present in a bitumen or a tar (these are chemically complex, very dark media, where the functional groups are present in very low concentrations). The method is being also used for the quantitative determination of the groups. A second class of solid reagents was devised to fractionate bitumens and tars into isofunctional sets of compounds. In these reagents a specific functional group is bound to a solid matrix in such a way that after proper procedure-the solid phase extraction method-a class of substances is extracted from the mixture; e.g., acylhydrazides bound to a polymetacrilate matrix have been used to separate aldehydes and ketones from the Irati oil shale bitumen. In a third approach, functional groups of kerogens have been determined by the functional group marker method, where a marker is incorporated to the kerogen by means of the reaction of a marked functional group reagent with the kerogen. The quantitative determination of the marker incorporated to kerogen is a measure of the (minimum) amount of that functional group. Fluorescent markers are presently being used (through microscopy) to define the topographical distribution of organic functional groups in kerogens (surface).

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GENERAL KINETIC MODEL OF OIL SHALE PYROLYSIS

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INTRODUCTION

Relatively simple effective kinetic expressions have been derived for oil evolution during pyrolysis of Green River oil shale: single first-order for slow and moderate heating rates (1, 2) and double first-order or single psuedo-nth-order for rapid isothermal pyrolysis (3-5). A number of workers (3, 4, 6-13) have investigated how secondary reactions (as influenced by pyrolysis heating rates, temperatures, residence times and pressure) can modify oil yield from that obtained under Fischer Assay (FA) conditions. They have found that the secondary reactions are very important, demonstrating that slow heating rates cause hetero-aromatic compounds in the oil to be converted to coke and that excessively high temperatures cause aliphatic structures to crack to gases.

While the qualitative aspects of oil-yield loss and quantitative relationships for some circumstances have been established, there is presently no mathematical formulation which can satisfactorily calculate the oil yield for any given oil shale heated under an arbitrary temperature-pressure-gas environment history. For example, Campbell et al. (7) demonstrated that the change in oil yield with pyrolysis heating rate is due to a competition between oil evaporation and coking. They developed a mechanism for oil coking that included an empirical rate constant for oil evaporation, but it cannot be used directly to calculate oil yields for conditions such as the interrupted heating schedules used by Stout et al. (6) or the elevated pressures used by Burnham and Singleton (12).

The mathematical model reported here is a first attempt at achieving our long-range goal of being able to calculate accurately the oil yield for any arbitrary pyrolysis conditions. As presently formulated, it is valid only for Green River oil shale, but it could be easily modified for other oil shales. A central feature of this model is that it divides the oil into 11 boiling-point fractions in order to treat evaporation more rigorously. This feature also allows cracking of heavy fractions to lighter fractions, enabling a calculation of the effect of pyrolysis conditions on the boiling-point distribution of the product oil. The model is tested under a wide range of pyrolysis conditions for which data are available in the literature. The model does very well generally, although certain limitations are demonstrated.

MODEL DESCRIPTION

The reactions defining the model and their associated rate constants are given in Table I. The properties of the oil components are given in Table II. Native bitumen is treated as being an initial oil content with properties described in Table II. The model assumes a uniformly reacting particle (no concentration or thermal gradients) and the absence of molecular oxygen. Formation of water from mineral dehydration and CO_2 from dolomite decomposition are included in order to properly calculate the residence time of the organic pyrolysis products inside the particle. The model also has the capability of an inert or H_2 sweep gas. Governing equations for the model are written as 67 first-order, nonlinear, ordinary equations specifying the rate of change of each gas, liquid and solid component in terms of the vaporization or chemical reactions. Some of the reactions are formulated to approach an equilibrium. This set of equations is solved simultaneously by LSODE (Livermore Solver for Ordinary Differential Equations) (14).

The kinetic parameters were taken as much as possible from the literature. Gas evolution kinetics, except those involving oil degradation, were taken (or derived in the case of CO_2) from the results of Campbell et al. (15) as modified by Huss and Burnham (16). For some reactions, it was necessary to use a distributed activation energy (17) in order to match observed results. Special numerical methods were developed for solving these reactions for arbitrary temperature history. We have also determined how these methods can be applied when the amount of a given component, such as a reaction intermediate, is not known at the beginning of the calculation.